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Article

***In situ* doping brushite on zinc manganese oxide toward enhanced water oxidation performance: Mimicry of an oxygen-evolving complex**

Miao Jiang, Junying Chen *, Yingwei Li #

State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China

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ABSTRACT

We report *in situ* doping of brushite on zinc manganese oxide (ZMO), fabricated by calcining a Mn(II) oxalate-impregnated metal-organic framework. The doping process was conducted in combination with the photocatalytic water oxidation reaction which was catalyzed by ZMO in neutral phosphate-buffered aqueous solution containing $[\text{Ru}(\text{bpy})_3]^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ and calcium(II) triflate salt, exhibiting greatly enhanced water oxidation performance with optimized turnover frequency of $0.18 \text{ mmol O}_2 \text{ mol Mn}^{-1} \text{ s}^{-1}$. Different analytical techniques indicated that photodeposited calcium-phosphate (CaP) acted as a co-catalyst to promote the O_2 evolution activity of ZMO. This system involved the use of manganese oxide and calcium ion, and the operation was conducted under ambient temperature and neutral conditions, thus, it efficiently mimicked the oxygen-evolving complex in photosystem II.

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1. Introduction

Producing renewable and clean energy is regarded as an effective strategy for meeting the energy needs of present and future generations [1]. Sunlight is the only source that provides sustainable and carbon-neutral energy to reduce the stress from the shortage of fossil fuels and environmental crises caused by the use of fossil fuels [2]. Consequently, researchers have long been focusing on the conversion and utilization of solar energy. One of the most promising strategies in pursuit of such ideal energy is water splitting to produce H_2 by either photo-induced routes or electronic techniques [3–10]. Howev-

er, a key challenge limiting the improvement of overall water splitting efficiency is the complicated and sluggish water oxidation reaction that involves the $4\text{H}^+/4\text{e}^-$ oxidation of two water molecules to dioxygen. Meanwhile, an efficient catalyst must tolerate the harsh conditions for water oxidation (*i.e.*, sufficient power), under which most functionalized moieties lose their activities for sustained water splitting [11]. In natural photosynthesis, sunlight is converted and stored via an oxygen-evolving complex (OEC) in photosystem II (PS II), which contains a Mn_4CaO_5 cluster surrounded by protein matrixes [12,13]. Inspired by nature's wisdom, numerous efforts have been devoted to developing an efficient artificial photosynthe-

* Corresponding author. Tel: +86-20-87113656; E-mail: chenjunying2010@sina.com

Corresponding author. Tel: +86-20-87113656; E-mail: liyw@scut.edu.cn

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sis system [14–19], especially where manganese oxide and calcium ions are involved. Mn chemistry exhibits multiple oxidation states and is capable of the Kok cycle of the natural PS II system. Ca^{2+} is widely recognized as a weak Lewis acid promoting the proton-coupled electron transfer (PCET) process between proteins and Mn-Ca cluster, and/or as the binding site for water molecular substitution [20]. In biomimetic studies, plenty of chemists have endeavored to develop calcium manganese oxide (CaMnO_x)-based systems, giving solid evidence for improved catalytic activity through the incorporation of Ca^{2+} in Mn oxides [20]. Li et al. [21] fabricated nanostructured non-crystalline CaMnO_x showing enhanced activity in water oxidation reactions for both chemical and photocatalytic systems. This work demonstrated that the disordered structure of CaMnO_x and a modest valence state of Mn were important factors for achieving high water oxidation activity. Several reports have provided similar insights into the relevance of highly crystalline structures of Mn oxides and their lower efficiencies in water oxidation compared to those of amorphous phases. Kurz and coworkers [22] synthesized layered Mn oxides containing a series of alkaline earth cations, e.g., K, Ca, Sr, and Mg. That with Ca incorporated reached the highest catalytic activity. Thapper's work studied the influence of phosphate ion on the construction of Mn oxide structures and valence state of Mn [23]. Considering the Angström-scale Mn_4CaO_5 cluster in OEC [24], the preparation of different phases of Ca-Mn oxides with ultra-small size and their use in photocatalytic water oxidation under neutral conditions would be of great interest.

In addition, metal-organic frameworks (MOFs) represent a class of coordination polymers with inherent features like ultrahigh porosity, enormous internal surface area, and flexibility [25–28]. Calcinating MOFs in atmosphere could afford neat metal oxides or metal oxides embedded in carbon matrices derived from organic units, owing to the periodical assembly of metal nodes and organic linkers in the frameworks. The resulting metal oxides may inherit some advantages from the pristine MOF such as enlarged surface area or ordered structures and thus exhibit excellent performances in various applications including catalysis, adsorption, as well as energy-related areas [29,30]. To the best of our knowledge, the use of MOF-templated transition metal oxides, especially Mn oxides, as photocatalysts for light-driven water oxidation has seldom been studied. Moreover, calcium-phosphate (CaP) including brushite is a class of inorganic minerals and normally non-toxic to living beings and the environment [31–34]. Their effects on water splitting reactions have not been studied before.

Herein, we report the design and synthesis of a MOF-templated Zn-Mn oxide (ZMO)-catalyzed water oxidation system to verify the role of calcium ion. The catalytic performances of photochemical water oxidation in phosphate-buffered neutral aqueous solution containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ were found to be 10-fold higher when the reaction was carried out in the presence of Ca^{2+} in comparison with those in the absence of Ca^{2+} . CaP was deposited *in situ* on ZMO during the photocatalytic reaction and played a key role in boosting the water oxidation reaction. Control experi-

ments with prolonged irradiation time demonstrated increased CaP contents in the resulting materials, which essentially influenced the catalytic activity. The ZMO material doped CaP *in situ* and its use in light-driven water oxidation involved the use of earth-abundant elements, ambient temperature, and neutral conditions, and thus could be regarded as an efficient functional model for OEC.

2. Experimental

2.1. General

Commercially available chemicals and reagents involved in this study were purchased from Shanghai Aladdin Reagent Co. Ltd and Macklin Biochemical Co. Ltd, China, and used without further purification unless otherwise indicated. $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) was purchased as chloride salt and metathesized in water by precipitation with excess NH_4PF_6 . The orange solid obtained was further recrystallized with ether from a minimum volume of acetone solution.

2.2. Synthesis

ZIF-8 was prepared according to the literature with a few modifications [35]. Typically, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (22.6 mmol, 6.7 g) was dissolved in 160 mL methanol. Another 160 mL methanolic solution containing 2-methylimidazole (180.3 mmol, 14.8 g) was added to the above solution with vigorous stirring. The mixture solution was kept stirring for 24 h. All operations were performed at room temperature. The product was separated by centrifugation and thoroughly washed twice with methanol, and finally dried at 50 °C overnight in a drying oven. The obtained ZIF-8 powders were further activated at 100 °C under vacuum for 10 h prior to use.

Zinc-manganese oxides (ZMOs) were synthesized by a conventional impregnation method followed by MOF-templated calcination. In a typical synthesis of ZMO, manganese(II) oxalate dehydrate (0.5 g) was dissolved in 20 mL ethanol. ZIF-8 powder (0.5 g) was added to the above solution. After stirring at room temperature for 2 h, the product was separated by centrifugation and washed thoroughly with ethanol and water. The resulting powders were dried in an oven at 80 °C overnight. After that, two-stage calcination was performed to obtain ZMO. The dry powders were first annealed at 400 °C for 8 h in nitrogen at a heating rate of 2 °C min^{-1} and cooled to room temperature. Then, the thermolysis temperature was elevated to 600 °C with the same heating program and maintained for 3 h in air flow. After cooling to ambient temperature, the produced powders were collected, dispersed in $\text{NH}_4\text{Cl}-\text{NH}_3 \cdot \text{H}_2\text{O}$ (5–2.5 mol L^{-1}) aqueous solution to remove excess ZnO, and washed with water. The final product was obtained after drying overnight in an oven at 80 °C. In addition, a series of ZMOs were prepared using the same procedure, changing only the time of the second calcination stage from 2 to 5 h or the amount of Mn oxalate from 0.1 to 0.7 g to obtain ZMOs with varied Zn/Mn ratios.

Mn_2O_3 -syn was synthesized according to the literature [36].

Mn₂O₃-1 was synthesized by calcinating Mn oxalate using the thermolysis program described for ZMO. Zn_xMn_yO_z was obtained by mixing zinc nitrate and manganese oxalate in the same ratio as that of ZMO, followed by thermolysis treatment using the heating program described above. The as-formed powders were dispersed in an NH₄Cl-NH₃·H₂O (5–2.5 mol L⁻¹) aqueous solution to remove possible ZnO and washed with water repeatedly.

2.3. Procedures of photocatalytic water oxidation and *in situ* doping brushite during the photocatalysis test

Photocatalytic oxygen evolution experiments were performed in a Labsolar-III AG photocatalysis system connected to gas chromatograph (GC, TECHCOMP 7900), which was equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column. Such tests were conducted in a 300-mL quartz reaction vessel containing 20 mg catalyst, 10 mmol L⁻¹ Na₂S₂O₈, 2 mmol L⁻¹ Ru(bpy)₃(PF₆)₂, and 10 mmol L⁻¹ Ca(CF₃SO₃)₂ in 100 mL phosphate buffer (0.25 mol L⁻¹ Na₂HPO₄-NaH₂PO₄ aqueous solutions, pH ~7). Reaction temperature was maintained using a low-temperature circulator at 25 °C. Reactants in the quartz vessel were degassed under vacuum for 20 min to remove all dissolved oxygen from the aqueous solution before doing the experiments. The quartz vessel was then irradiated from the top window with a continuous output Xe lamp (300 W, Microsolar 300). The amounts of O₂ evolved were determined by external standard method either through online GC injection process every 30 min or by manual injection of a quantified gas phase from the headspace of the reactor every 5 min with high purity argon gas as carrying gas. CaP was deposited on ZMO catalyst during the photocatalytic reaction. After one cycle of the photocatalysis test, the catalyst was collected and washed with acetone and deionized water repeatedly, and dried overnight at 80 °C. The final material was denoted ZMO-insitu.

2.4. Photodeposition of brushite on ZMO before water oxidation test

The photodeposition of brushite before the water oxidation test was executed by the irradiation of a solution containing 20 mg ZMO and 10 mmol L⁻¹ Ca(CF₃SO₃)₂ in 100 mL phosphate buffer (0.25 mol L⁻¹ Na₂HPO₄-NaH₂PO₄ aqueous solutions, pH ~7) for a certain time (*e.g.*, 15, 30, 45, and 60 min). The catalyst, denoted CaP@ZMO-*x* (*x* = 15, 30, 45, and 60), was filtered, washed with acetone and deionized water, and dried overnight at 80 °C. The amounts of CaP doped on ZMO were normalized to the Ca contents in the as-formed materials by AAS. To confirm that the deposition was induced by photo-irradiation, this procedure was also performed in the dark. The resulting material, denoted CaP@ZMO-0, was collected, washed, dried, and characterized.

2.5. Characterization

Powder X-ray diffraction (XRD) patterns of the samples

were recorded on a Rigaku diffractometer (D/MAX/III A, 3 kW) using Cu-K_α radiation (40 kV, 30 mA, λ = 0.1543 nm). Thermogravimetric (TG) curves were recorded on an SDT-Q600 instrument from room temperature to 900 °C at a heating rate of 10 °C min⁻¹ under air flow. The zinc, manganese, and calcium contents in each sample were measured quantitatively by atomic absorption spectroscopy (AAS) using a HITACHI Z-2300 instrument. The BET surface areas and pore sizes were obtained from the N₂ adsorption-desorption isotherms measured on a Micromeritics ASAP 2020M instrument at -196 °C. Before the measurements, the samples were degassed at 100 °C for 6 h. X-ray photoelectron spectroscopy (XPS) measurement was performed using a Krotos Axis Ultra DLD system with base pressure of 10⁻⁹ Torr. The surface morphologies of the materials were investigated using a high-resolution scanning electron microscope (SEM, MERLIN of ZEISS) equipped with an energy dispersive X-ray spectrometer (EDS). The structure and elemental distribution were determined with a high-resolution transmission electron microscope (TEM, JEOL, JEM-2100F) with an EDX analysis system (Bruker Xflash 5030T) operated at 200 kV.

3. Results and discussion

3.1. Characterization of the corresponding materials

MOF-templated synthesis of ZMO is illustrated in Scheme 1. The pristine MOF, ZIF-8, was prepared according to literature from the reaction of Zn²⁺ and 2-methylimidazole. The successful formation of dodecahedral ZIF-8 with smooth rhombic surfaces and mean particle size of around 200–300 nm was confirmed from SEM images and XRD patterns (Fig. 1) [35]. Its thermal behavior was measured by TG, which suggested a well-maintained MOF structure until the thermolysis temperature was above 400 °C in air (Fig. S1).

After a conventional impregnation procedure with manganese oxalate, the resulting material was calcined using a two-stage temperature-elevating program. The product from the first stage was analyzed by XRD and TEM measurements, showing similar XRD patterns as that of pristine ZIF-8 (Fig. S2) and well-preserved dodecahedral morphology with some perceived particles on the surfaces (Fig. S3(a)). High-resolution TEM (HRTEM) image of these particles revealed an interplanar

Scheme 1. Schematic illustration of the preparation of ZMO and *in situ* doping of CaP.

Fig. 1. SEM image (a) and XRD patterns (b) of ZIF-8 crystals.

distance of 0.311 nm, in good agreement with the lattice spacing of the {110} plane of MnO_2 (Fig. S3(b)). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and corresponding elemental mapping images clearly indicated the loading of manganese oxide on ZIF-8 (Fig. S3(c)–(i)). When the second stage of thermolysis was performed at an elevated temperature of 600 °C under air, MnO_2 was reduced to Mn_2O_3 . Similar phase transformation of Mn oxides during annealing processes have been reported previously [37,38]; meanwhile, the MOF structure totally collapsed

to provide ZnO, which further reacted with Mn_2O_3 from MnO_2 to form ZnMn_2O_4 . XRD results indicated that the as-formed material was a mixture of ZnMn_2O_4 and Mn_2O_3 with manganese oxide being the dominant phase (Fig. 2(a)). To verify the electronic structure and chemical valence of Mn in ZMO, XPS analysis was conducted, as shown in Fig. 2(b) and (c). The XPS survey spectrum confirmed the existence of Zn, Mn, and O (Fig. 2(b)). The peaks at 641.7 and 653.5 eV could be assigned to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively; the binding energy difference of 11.8 eV was consistent with that of Mn_2O_3 (Fig. 2(c)). The-

Fig. 2. (a) XRD patterns of ZMO (red line) and ZMO-insitu (blue line); XPS spectra of full scan (b) and Mn $2p$ region (c) of ZMO; (d) Nitrogen adsorption-desorption isotherms and pore size distribution (inset) curves of ZMO and ZMO-insitu.

peaks at ~ 1044.57 and 1021.47 eV, attributed to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, were the characteristics of Zn^{2+} (Fig. S4); the energy difference of 23.1 eV implied the existence of ZnMn_2O_4 phase. Fig. 2(d) shows the N_2 adsorption-desorption isotherms of ZMO measured at liquid nitrogen temperature. An obvious hysteresis loop at p/p_0 of 0.4–1.0 was detected, showing typical type-IV adsorption curves for meso- and/or macroporous structures. The BET surface area of ZMO was measured to be $30.67 \text{ m}^2 \text{ g}^{-1}$. In addition, results of elemental analysis and AAS measurements for the corresponding materials are listed in Table 1. Both Zn content and Zn/Mn ratio revealed the dominance of Mn_2O_3 phase over ZnMn_2O_4 . The low content of Zn in this material could be due to easy removal of ZnO with thermolysis and dissolution treatments.

TEM image of representative ZMO showed irregularly shaped nanoparticles (Fig. 3(a)) with average crystalline size of $30 \pm 5 \text{ nm}$, calculated with the Debye-Scherrer formula $D = k\lambda/\beta\cos\theta$, where D is the mean crystalline size, k is the shape factor (0.89), λ is the X-ray wavelength ($1.543 \text{ \AA}$), β is the full width at half maximum (FWHM) of the corresponding diffraction line, and θ is the diffraction angle. HRTEM analysis revealed interplanar spacings of 0.247 and 0.272 nm (Fig. 3(b)), in accordance with the {211} plane of ZnMn_2O_4 (hetaerolite, JCPDS 24-1133) and {222} plane of Mn_2O_3 (bixbyite, JCPDS 41-1442). EDX mapping images of ZMO, along with the HAADF-STEM image, confirmed that Mn, Zn, and O elements were well-distributed within the material (Fig. 3(c)–(f)).

In addition, a series of Zn-Mn oxides was prepared by annealing Mn oxalate-impregnated ZIF-8 under varied conditions.

Table 1

Characterization results and water oxidation performances of the catalysts.

Catalyst	Mn (%)	Zn ^a (%)	O ^b (%)	TON ^{c,e}	TOF ^{d,e}	A_{BET} (m^2/g)
Mn_2O_3 -syn	69.60 ^f	0.00	30.40	0.042	0.023	16.82
Mn_2O_3 -1	69.60 ^f	0.00	30.40	0.000	0.00	–
$\text{Zn}_x\text{Mn}_y\text{O}_z$	69.47 ^a	0.82	29.71	0.0035	0.0020	–
ZMO	43.94 ^a	4.38	51.68	0.32	0.18	30.67

^a Measured by AAS. ^b Calculated. ^c Defined as moles of evolved O_2 in the first 30 min per mole Mn. ^d Defined as millimoles of evolved O_2 in the first 30 min per mole Mn per second ($\text{mmol}_{\text{O}_2}/\text{mol}_{\text{Mn}} \text{ s}$). ^e Reaction conditions: 20 mg catalyst; $[\text{Ru}(\text{bpy})_3]^{2+}$ 2.0 mmol L^{-1} ; $\text{S}_2\text{O}_8^{2-}$ 10.0 mmol L^{-1} ; Ca^{2+} 10 mmol L^{-1} ; pH ~ 7 , 0.25 mol L^{-1} phosphate buffer; total volume: 100 mL. ^f Normalized as the Mn content in Mn_2O_3 .

The XRD patterns were all similar to that of ZMO, consisting of a mixture of Mn_2O_3 and ZnMn_2O_4 phases (Fig. S5). For further comparison, several materials containing Mn_2O_3 and/or Zn ions were synthesized and used for photocatalytic water oxidation. Manganese oxalate was annealed under conditions identical to that of the synthesis of ZMO. The resulting material was well characterized. Its XRD patterns were in agreement with Mn_2O_3 (JCPDS 41-1442), and thus this material was denoted Mn_2O_3 -1 (Fig. S6). Moreover, Mn_2O_3 was also prepared through a conventional synthetic method, denoted Mn_2O_3 -syn. The corresponding physiochemical properties are shown in Tables 1 and S6. When a mixture of zinc nitrate and Mn oxalate was annealed under the same condition, the resulting material was analyzed to contain Mn_2O_3 (JCPDS 41-1442) as the dominant

Fig. 3. TEM (a), HRTEM (b), HAADF-STEM (c), and EDX mapping images (d–f) of ZMO.

phase by XRD analysis and a very small amount of ZnMn_2O_4 was also involved (Fig. S6), suggesting that simply annealing a mixture of two metal salts was not a useful strategy for affording Zn-Mn oxides.

3.2. Photocatalytic water oxidation for O_2 evolution and photodeposition of CaP on ZMO

Light-driven water oxidation reactions were conducted in a well-established $[\text{Ru}(\text{bpy})_3]^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ system in neutral phosphate buffer aqueous solution, where $[\text{Ru}(\text{bpy})_3]^{2+}$ was excited by irradiation of UV and/or visible light to form its excited radical state, which could be further oxidized by $\text{S}_2\text{O}_8^{2-}$ to give $[\text{Ru}(\text{bpy})_3]^{3+}$, the primary oxidant participating in ZMO-catalyzed water oxidation [20,39]. Initial assessments demonstrated that the ZMO catalyst, light-irradiation, photosensitizer, and sacrificial electron acceptor were all necessary factors for photocatalytic reaction. In addition, it is known that water oxidation in the $[\text{Ru}(\text{bpy})_3]^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ system is highly dependent on the pH value of the applied solution. The oxidant, $[\text{Ru}(\text{bpy})_3]^{3+}$, is more stable under acidic conditions, *i.e.*, $\text{pH} < \sim 4$; whereas under basic conditions, water oxidation activity could be accelerated due to fast reduction of the Ru^{3+} ion [20,39]; besides, natural photosynthesis generates O_2 from neutral water. The conditions for ZMO-catalyzed water oxidation were optimized based on the above considerations, including the pH of the buffer, the concentration of catalyst, the ratio of the photosensitizer versus the electron acceptor, and the methods used in catalyst synthesis (Figs. S7–S12). Under optimized conditions, which were neutral phosphate buffer aqueous solution, $[\text{Ru}(\text{bpy})_3]^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ (2–10 mmol L^{-1}), and 0.2 g L^{-1} ZMO, the amount of O_2 evolved increased approximately linearly for the first 30 min (Fig. 4); the turnover frequency (TOF) based on the amount of O_2 evolved in the first 30 min was calculated to be 0.018 $\text{mmol}_{\text{O}_2} \text{mol}_{\text{Mn}}^{-1} \text{s}^{-1}$. Interestingly, the catalytic activity could be further enhanced significantly when 10 mmol L^{-1} calcium triflate was added at the beginning of the above reaction. The highest TOF of 0.18 mmol_{O_2}

Fig. 4. Time course of O_2 evolution in photocatalytic water oxidation using ZMO as photocatalyst in the absence and presence of Ca^{2+} (10 mmol L^{-1}). Reaction conditions: 20 mg ZMO; $[\text{Ru}(\text{bpy})_3]^{2+}$ 2.0 mmol L^{-1} ; $\text{S}_2\text{O}_8^{2-}$ 10.0 mmol L^{-1} ; $\text{pH} \sim 7$, 0.25 mol L^{-1} phosphate buffer; total volume: 100 mL.

$\text{mol}_{\text{Mn}}^{-1} \text{s}^{-1}$ was obtained, 10-fold higher than that of ZMO without Ca^{2+} . Although a similar linear relationship of reaction time *versus* amount of O_2 was detected for the first 25 min, the reaction terminated after 35 min (Fig. 4).

To explore the greatly enhanced water oxidation performance and the role of Ca^{2+} , the final powder, ZMO-insitu, and reaction solution were analyzed. XRD patterns of ZMO-insitu were consistent with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (brushite, JCPDS 09-0077); the peaks for Mn_2O_3 and ZnMn_2O_4 were almost undetectable, probably owing to the high crystallinity and large amount of CaP formed *in situ* (Fig. 2(a)). TEM images also confirmed the existence of CaP, showing nanorod crystals of monoclinic brushite wrapping around ZMO (Fig. S13). After washing repeatedly with water and organic solvents, the as-formed free brushite crystals were mostly washed out. The TEM image of ZMO-insitu after washing procedure is shown in Fig. 5(a). The HRTEM image showed lattice spacings of 0.272 and 0.762 nm, which could be assigned to the {222} and {020} planes of

Fig. 5. TEM (a), HRTEM (b), HAADF-STEM (c), and EDX mapping images (d–h) of ZMO-insitu.

Mn₂O₃ (bixbyite) and CaHPO₄·2H₂O (brushite) phases, respectively (Fig. 5(b)). The HAADF-STEM image of the edge of the ZMO particle and the corresponding element mapping results clearly showed the homogeneous distribution of Mn, Zn, O, Ca, and P elements, indicating that brushite was successfully loaded on the catalyst at high amounts during the photocatalytic reaction (Fig. 5(c)–(h)). The BET surface area decreased significantly to 17.71 m² g^{−1}, implying the occupation of CaP on the surface and/or in the pores of ZMO (Fig. 2(d)). These results confirmed *in situ* doping of CaP on ZMO, which could be the primary reason for the notably promoted photocatalytic activity. However, when ZMO-*in situ* was used in another reaction cycle of water oxidation, it showed ignorable catalytic activity. The large excess of free CaP could cover the catalytically active sites of ZMO, leading to deactivation of ZMO in the water oxidation reaction. In addition, the pH of the reaction solution changed slightly to 6.3 after the water oxidation reaction, indicating that phosphate anions (HPO₄^{2−} and H₂PO₄[−]) acted as proton acceptors; protons were released during the water oxidizing process, and its buffering capacity provided a repair mechanism, similar to the role of Lewis basic amino acids in OEC for proton transport in natural photosynthesis. The decrease in pH may also be related to the consumption of phosphate anion to form CaP *in situ*.

To verify the influence of irradiation time and loading content of CaP on ZMO-catalyzed water oxidation, a series of control experiments was conducted by varying the important parameters. First of all, the blank test done under optimal experimental condition without the ZMO catalyst showed no photocatalytic activity, although free nanorod crystals of CaP were generated. Second, several CaP@ZMO catalysts were prepared by immersing ZMO in phosphate buffer containing 10 mmol L^{−1} Ca²⁺, followed by irradiation with a Xe lamp for a certain time. The resulting powders were collected and washed for further characterization and water oxidation experiments in a [Ru(bpy)₃]²⁺-Na₂S₂O₈ system without added Ca²⁺. The XRD results are shown in Fig. 6. In the case of CaP@ZMO-0, there was neither an obvious peak for CaP in the XRD analysis nor significant enhancement of catalytic activity in the water oxidation

reaction; the XRD patterns were mainly attributed to the original ZMO catalyst. This result confirmed that the deposition of CaP on ZMO was actually induced by light irradiation. An increased amount of CaP was detected with increasing irradiation time, which was also consistent with the AAS results (Table S1). The deposition of metal phosphates had been manifested through electronic or thermal treatments previously [40–42].

Accordingly, the photocatalytic activities were enhanced largely by CaP-doping relative to that of bare ZMO. However, the water oxidation performances of the resulting CaP@ZMO-*x* materials showed a volcano-type relationship with CaP content (Fig. 7). CaP@ZMO-30 was the most active in photocatalytic water oxidation, producing 14.51 μmol O₂ in the first 30 min. Prolonging the irradiation time to 1 h could have had a negative effect on the catalytic activity. CaP@ZMO-60 showed almost no activity in water oxidation. The XRD patterns of CaP@ZMO-60 were similar to that of ZMO-*in situ* with almost no detectable peaks of ZMO (Fig. 6). These results demonstrated that CaP in its free form was inactive in water oxidation reaction, and only those that were deposited on ZMO catalyst were of important for accelerating the water oxidation activity.

Although the total amount of O₂ evolved on CaP@ZMO-30 was much less than that of the ZMO doped CaP *in situ*, it was quite understandable since there was a dynamic equilibrium between Ca²⁺ and HPO₄^{2−} in the solution and the formation of CaP. Without continuous supply of Ca²⁺ and HPO₄^{2−}, the doped CaP partially dissolved under irradiation during photocatalytic water oxidation, leading to an increase in the concentrations of both the cation and anion in the local microenvironment, which further gathered to form the Ca₃(PO₄)₂·*x*H₂O phase in the presence of hydroxide ions derived from water splitting on the surface of ZMO, and thus, hindered O₂ formation. The overall reaction is complicated, and some possible reactions are:

Fig. 6. XRD patterns of CaP@ZMO-*x*, where *x* = 0 (a), 15 (b), 30 (c) and 60 (d).

Fig. 7. Water oxidation performance of CaP@ZMO-*x*, where *x* = 0 (a), 15 (b), 30 (c), and 60 (d). Reaction conditions: 20 mg ZMO pre-deposited with different amounts of CaP; [Ru(bpy)₃]²⁺ 2.0 mmol L^{−1}; Na₂S₂O₈ 10.0 mmol L^{−1}; pH ~7, 0.25 mol L^{−1} phosphate buffer; total volume: 100 mL.

The $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ phase was detected in the XRD analysis of CaP@ZMO-30 after one cycle of water oxidation reaction, as shown in Fig. S14, while the patterns of CaP disappeared almost completely. Moreover, the resulting $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ loading on ZMO showed negligible impact on accelerating the water oxidation activity of the catalyst, as evident from the amount of evolved O_2 in the second reaction cycle of CaP@ZMO-30, which was nearly the same as that of bare ZMO (Table S1).

It was noteworthy that both ZMO-insitu and CaP@ZMOs showed inferior reusabilities because of the large excesses of free CaP covering the active sites of ZMO in the former, and phase-transformation of calcium phosphate in the latter. Further attention to the use of brushite as co-catalyst to boost the photoactivity of a catalyst needs to be paid on changing the balance between the supplementary of calcium salts and the prohibition of undesired phase-transformation of calcium-phosphates.

3.3. The effect of Zn^{2+} in photocatalytic water oxidation

Zn^{2+} derived from MOF precursor also positively influenced the catalytic activity. When Mn_2O_3 -1, Mn_2O_3 -syn, and $\text{Zn}_x\text{Mn}_y\text{O}_z$ were investigated in photocatalytic water oxidation under identical conditions to those of ZMO, Mn_2O_3 -1 was found inactive with no detectable O_2 evolution while Mn_2O_3 -syn and ZnMnO_x were much less efficient catalysts than ZMO in the presence of Ca^{2+} (Table 1). Although a series of Zn-Mn oxides with different Zn/Mn ratios were prepared and used as photocatalysts in water oxidation, the correlation between the activity and the amount of Zn^{2+} or between the activity and the surface area was not convincing. The photocatalytic activity of this reaction system might be affected by several key parameters including the surface area, the concentration of alkaline metals, and the phase composition of the catalyst. Bringing ZIF-8 in the synthesis of metal oxide could not only afford a material of mixed transition metal oxide with a larger surface area (Table 1)—which counts for better catalytic activity—but also introduce Zn^{2+} (a weak Lewis acidic metal ion but stronger than Ca^{2+}) to the resulting material. It was reported that Zn^{2+} was able to bind with metal-oxygen complexes, e.g., Fe(IV)-oxo, Fe(III)-peroxo, and Mn(IV)-oxo, and significantly influence the reactivities of electron transfer reactions [43–45]. In addition, introducing a small amount of alkaline metal into the layer matrix between graphene and semiconducting material could facilitate the transfer efficiency of photogenerated charge carriers, leading to significantly improved photoactivity [46]. Since water oxidation reaction proceeds through multiple proton-coupled electron transfer processes, the vital roles of redox-inactive metal ions such as Zn^{2+} , Ca^{2+} , and Sr^{2+} in water splitting are highly convincing. Interestingly, considering that Mn_2O_3 -1 was inactive and ZMO was a mixture of a dominant phase of Mn_2O_3 and low amount of ZnMn_2O_4 (normalized to the Zn content in AAS results), the amounts of Mn in its active form could be distinctly lower than those used in calculating TOFs. Therefore, the actual TOF based on Mn content in the form of

ZnMn_2O_4 could be much higher than $0.18 \text{ mmol}_{\text{O}_2} \text{ mol}_{\text{Mn}}^{-1} \text{ s}^{-1}$ reported here.

4. Conclusions

We reported the fabrication of MOF-template zinc manganese oxide and its use in photocatalytic water oxidation in neutral phosphate-buffered aqueous solution containing $[\text{Ru}(\text{bpy})_3]^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$. The water oxidation performance of ZMO could be significantly improved in the presence of calcium ion. A variety of analytical techniques indicated that brushite was doped *in situ* on ZMO during the water oxidation process, acting as co-catalyst to promote O_2 evolution activity. We also discussed the positive influence of Zn ion derived from ZIF-8 on the photocatalytic water oxidation activity. Our findings demonstrated that calcium phosphate-doped Zn-Mn oxide featured as an effective functional model of the oxygen-evolving complex in photosystem II.

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Graphical Abstract

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In situ doping brushite on zinc manganese oxide toward enhanced water oxidation performance: Mimicry of an oxygen-evolving complexMiao Jiang, Junying Chen*, Yingwei Li*
South China University of Technology

Brushite was *in situ* doped on MOF-templated zinc-manganese oxide via photodeposition in neutral water containing phosphate and calcium(II) ions, and was responsible for enhanced photocatalytic water oxidation performance.

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锌锰氧化物原位负载磷酸氢钙以提高水氧化性能：一种放氧化合物的模型

江 森, 陈俊英*, 李映伟#

华南理工大学化学与化工学院, 制浆造纸工程国家重点实验室, 广东广州510640

摘要: 能源已经成为人类赖以生存和社会发展的物质基础。随着社会飞速发展和人口迅速增长, 全球能源消耗逐年激增。资料显示, 天然气、石油、煤这三种化石能源仍然是全球主要能源。众所周知, 化石燃料不可再生, 已探明储量的化石燃料仅可供人类使用100–200年。而且, 化石燃料的燃烧会带来严重的环境污染和CO₂等温室气体的排放。这些问题促使人类寻找开发其它可再生新型能源。而利用太阳光就是很重要的一个可行方案。

光合作用整个过程主要涉及到光系统I(PS I)和光系统II(PS II)。在PS I中, 太阳光激发后会有一个电子的转移, 使得NADP⁺被还原为NADPH, 然后NADPH会和CO₂作用产生糖类。在PS II中, 水通过Mn₄CaO₅簇被氧化为氧气。而人工光合作用

用则是将 H_2O 和 CO_2 转化为 O_2 和其他含碳化合物或者是直接将 H_2O 光解为 H_2 和 O_2 。通过人工模拟光合作用,将水裂解为 H_2 和 O_2 被视为更为直观可行的解决能源的方法。其中,水氧化是一个复杂缓慢的过程,也是水全裂解的瓶颈。因此设计合成高效水氧化催化剂是提高人工光合作用性能的关键。

自然界光合作用中水氧化反应进行的场所是PSII的放氧复合体(OEC),其活性中心是被蛋白质环境包围的 Mn_4CaO_5 簇。2011年,Shen等报道了解相率为1.9 Å的PS II的X-射线晶体结构,在电子密度图上清楚无疑地锁定了 CaMn_4O_5 簇中各个金属的位置以及它们周围的配体的位置。三个Mn、一个Ca、四个O组成一个立方烷的骨架结构,四号Mn通过氧桥键与立方烷中的一个Mn原子相连,该Mn原子上有两个水分子,另外两个水分子配位在Ca上。整个 CaMn_4O_5 簇周围的氨基酸起到了稳定OEC的作用。人们一般认为,Mn和Ca是PS II中WOC必不可少的辅助因子。大量实验表明,钙是WOC的功能性和稳定性中必不可少的存在。

锰和钙不仅在地球上资源丰富,而且于环境无害,因此是一种极具吸引力的水氧化催化剂。基于此,本文通过焙烧浸渍锰盐的金属有机骨架材料(MOF),成功合成出一种锌锰氧化物(ZMO),并在含三氟甲磺酸钙的中性磷酸缓冲溶液中进行的光催化水氧化反应的同时原位负载钙磷石(CaP),展现出TOF高达 $0.18 \text{ mmolO}_2 \text{ molMn}^{-1} \text{ s}^{-1}$ 的优良性能。通过X射线粉末衍射、扫描电镜、透射电镜、原子吸收、X射线光电子能谱、热重、 N_2 吸附-脱附等温线等对催化剂的物相、颗粒大小、元素组成以及比表面积等进行了一系列表征,证明了CaP作为助催化剂提高了锌锰氧化物的光催化产氧性能。该催化剂主要使用了过渡金属锌、锰,以及钙元素,并且在常温和中性条件下使用,因而可以被视为一种有效模拟OEC的功能型化合物。

关键词: 锌锰氧化物; 钙磷石; 金属有机框架; 水氧化; 放氧复合体

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*通讯联系人. 电话: (020)87113656; 电子信箱: chenjunying2010@sina.com

#通讯联系人. 电话: (020)87113656; 电子信箱: liyw@scut.edu.cn

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